Recycling Heterogenous Catalysts for Multi-Batch Conjugated Polymer Synthesis via Direct Arylation Polymerization (DArP)

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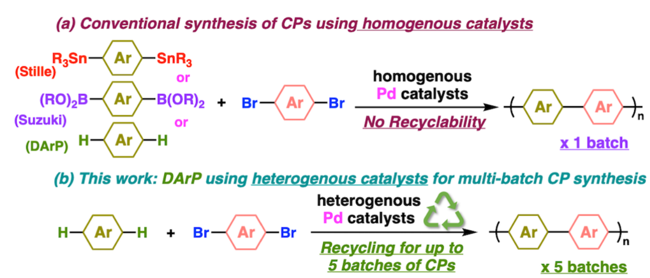
ABSTRACT: Despite the inherent sustainability Direct Arylation Polymerization (DArP) offers through a C-H activation pathway, the use of expensive homogenous Pd catalysts remains problematic for large-scale conjugated polymer (CP) synthesis. Herein, the first report on the recycling of heterogenous catalysts for CP synthesis using DArP is presented. We found Silia*Cat*® Pd-DPP to be a highly efficient and recyclable catalyst for multi-batch CP synthesis providing CPs with molecular weights (M_n) up to 82 kg/mol even after being recycled 3 times. Batch-to-batch variations were further optimized to afford up to 5 batches of polymers with M_n of 25±2.5 kg/mol without structural disparity. Significantly, this work discloses among the most sustainable CP synthesis protocols to date and presents the critical concept of catalyst-recycling to the important field of organic semiconducting polymers, which potentially enables access to truly low-cost flow chemistry for industrial-scale CP synthesis.

Conjugated polymers (CPs) are flexible low-cost materials that attract great interest for a wide range of applications, such as organic photovoltaics (OPVs), organic light emitting diodes (OLEDs), electrochromics, and bioelectronics.[1–5] Recently, with progress towards commercialization and the emergence of large-area roll-to-roll processing, the demand for industrial-scale CP synthesis has grown rapidly.[6,7] To synthesize CPs, the Stille polycondensation is one of the most widely employed traditional cross-coupling methods, which however has significant drawbacks. Specifically, the generation of stoichiometric, highly toxic organotin byproducts and a multistep preparation of unstable stannylated monomers, makes Stille impractical for the large-scale synthesis of CPs.[8]

In recent years, Direct Arylation Polymerization (DArP) has emerged as a facile synthetic tool for the preparation of high-quality CPs through an atom-economical C-H activation pathway, alleviating the need for hazardous, pyrophoric reagents and reducing toxic waste production (Scheme 1a).[8–10] Recent advances in replacing traditional, hazardous solvents with bio-renewable green alternatives such as cyclopentyl methyl ether (CPME) and p-cymene have further enhanced the sustainability of DArP protocols.[11,12] However, among the most crucial limitation of prevailing DArP methods is the catalyst, which is almost exclusively based on the rare and expensive metal Pd.[13] While ongoing efforts focus on developing earth-abundant metals, such as Cu, for DArP,[14,15] heterogenous catalysts offer another avenue to potentially extend the lifetime of a Pd catalyst beyond a single use, which could significantly reduce the cost of large-scale CP synthesis.[16] Although the utility of heterogenous catalysts in DArP has been demonstrated in a few cases, the recyclability of these catalysts has never been tested beyond the initial batch of CP.[17–20] Significantly, we address this important limitation of DArP here by disclosing the first report on the recycling of heterogenous catalysts for the synthesis of up to 5 batches of CPs via DArP (Scheme 1b), with minimization of batch-to-batch variation (M_n of 25±2.5 kg/mol across all 5 batches). The novel protocol developed herein marks a major breakthrough for CP synthesis and marks an enabling step toward the inexpensive, scalable preparation of semiconducting polymers.



Scheme 1. Brief summary of Pd-catalyzed CP synthesis.

Homogenous Pd catalysts on which most current DArP protocols are reliant (Scheme 1a), such as $Pd(OAc)_2$ and $Pd_2(dba)_3$, have several shortcomings, including the lack of recyclability of the expensive catalysts and Pd contamination in the synthesized CPs, which significantly hampers performance in organic electronics.[21,22] Conversely, we identified Silia*Cat*® DPP-Pd, a diphenylphosphine-based Pd(II) species covalently bound to an organosilica matrix, as a promising heterogenous catalyst due to its excellent performance in molecular aryl-aryl cross-coupling reactions such as Suzuki and Heck with low Pd-leaching.[23–26] Moreover, the recyclability of Silia*Cat*® DPP-Pd has previously been showcased in various small-molecule Stille and Suzuki coupling reactions, and further extended to large-scale synthesis in commercial flow reactors.[25–27] Although

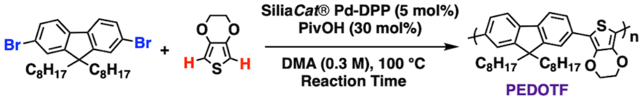
Table 1. Initial testing of the recyclability of Silia*Cat*® Pd-DPP using DArP conditions depicted in Scheme 2.[a]

entry[b]	number of cycle	reaction time (h)	catalyst recycled (%)[c]	M_n (kg/mol)[d], Đ[d]	yields (%)
1	cycle 1 (initial)	0.5	-	29, 2.0	94
2	cycle 2	0.5	97	23, 1.8	89
3	cycle 3	0.5	92	6.1, 1.7	72
4	cycle 4	3	88	33, 1.9	93
5	cycle 1 (initial)	0.5	-	27, 2.0	96
6	cycle 2	0.5	98	21, 2.3	93
7	cycle 3	1.5	96	26, 2.0	90
8	cycle 4	3	91	63, 1.8	95
9	cycle 5	24	93	12, 1.9	89

[a] All polymerizations were conducted using the general conditions shown in Scheme 2. For Cycles 2-4, the amounts of monomers were re-adjusted to keep the catalyst loading (5 mol%) and monomer concentration (0.3 M) constant. See SI for experimental details. [b] Entries 1-4, 5-9 are two separate rounds of catalyst-recycling experiments. [c] Determined based on the mass of recovered catalyst from the previous cycle. [d] Estimated by GPC (140 °C, 1,2,4-trichlorobenzene) calibrated with polystyrene standards.

Leclerc et al. have previously demonstrated the high reactivity of this heterogenous catalyst in DArP using Ozawa-derived conditions (i.e., in non-polar solvents),[8,18] our preliminary efforts revealed that the recovered Silia*Cat*® DPP-Pd was not reusable after the initial polymerization under similar conditions (see SI for details). This may be attributed to the longer reaction time usually required for these polymerizations (24 hours or more) compared to those for small-molecule cross-coupling reactions (~30 mins),[25,26] which likely results in significant leaching of Pd from the solid support suppressing the catalytic activity of the recovered Pd species.[26,28] Furthermore, the use of an additional ligand in Ozawa-derived DArP conditions (P(o-anisyl)$_3$) may sequester Pd from the solid support and contribute to the Pd-leaching.[24]

Poly[(3,4-ethylenedioxythiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] (PEDOTF) is an important candidate for electrochromics and OLEDs with excellent electroluminescent properties.[29] Moreover, Kanbara et al. have shown that short reaction times (30 mins for microwave heating or 3-6 hours for conventional heating) are viable for the synthesis of PEDOTF via DArP using Fagnou-derived conditions, which lead to higher reactivity due to the use of polar, coordinating solvents, making this polymer an ideal target for testing the recyclability of heterogenous catalysts for CP synthesis.[30,31] These Fagnou-derived conditions are highly efficient for the C-H activation of electron-rich thiophenes such as 3,4-ethylenedioxythiophene (EDOT), but unsuitable for electron-deficient thiophene monomers such as thieno[3,4-c]pyrrole-4,6-dione (TPD).[32] Welch et al. utilized 5 mol% of Silia*Cat*® DPP-Pd, along with K_2CO_3 as the base, pivalic acid (PivOH) as an additive, and N,N-dimethylacetamide (DMA) as the solvent at 100 °C for small-molecule direct



Scheme 2. Synthesis of PEDOTF using Silia*Cat*® Pd-DPP as the heterogenous catalyst.

arylation of thiophene-based substrate.[26] These conditions are highly similar to those employed by Kanbara et al. for the preparation of PEDOTF using DArP.[30,31] Therefore, we adopted these conditions for the synthesis of PEDOTF via DArP using Silia*Cat*® DPP-Pd and the examination of its recyclability (Scheme 2).

The high reactivity of Silia*Cat*® DPP-Pd in this model system was first realized by affording PEDOTF with M_n of 29 kg/mol and yield of 94% in only 0.5 h of reaction time (Table 1, entry 1). A large scale polymerization (increased from 0.4 mmol to 2 mmol of monomers) was performed using the same reaction conditions, which afforded gram-scale production of PEDOTF (0.92 g) with a better M_n of 42 kg/mol (Đ = 2.5) and a good yield of 87% (see SI for details), demonstrating the industrial scalability of these DArP conditions. These results demonstrate that Silia*Cat*® DPP-Pd is highly efficient with DArP by enabling a shortened reaction time without microwave assistance, compared to conventional homogenous Pd catalysts such as $Pd(OAc)_2$ (affording PEDOTF with M_n of 14.9 kg/mol after 3 h of conventional heating under otherwise the same reaction conditions, reported by Kanbara et al.).[30,31] The high reactivity of Silia*Cat*® DPP-Pd compared to homogenous $Pd(OAc)_2$ is also consistent with findings by Welch et al. in small-molecule studies.[26] The heterogenous catalyst from this reaction was easily isolated from the polymerization mixture through a simple filtration, washed and dried (see SI for experimental details), and subjected to the next cycle (Table 1, entry 2). This second cycle of polymerization using the recycled Silia*Cat* DPP-Pd from the first run still exhibited excellent catalytic activity by providing PEDOTF with good M_n of 23 kg/mol and yield of 89% in only 0.5 h. Furthermore, we concluded that although a loss of catalytic activity was observed during the third cycle (Table 1, entry 3) giving a lower M_n (6.1 kg/mol) and yield (72%), an extended reaction time from 0.5 h to 3 h effectively promoted the reaction with high M_n (33 kg/mol) and yield (93%) for the fourth cycle (Table 1, entry 4). Importantly, it is worth-noting that we were able to recycle large majorities (88.3-96.6%) of the catalyst for the following cycles after each polymerization.

The effect of carboxylic acid additives was also investigated (Table S1). Interestingly, we found that replacing PivOH with the sterically bulkier neodecanoic acid (NDA) resulted in lower M_n (19 kg/mol, 8.1 kg/mol, 4.1 kg/mol, respectively) for the first three cycles with short reaction times (0.5 h) (Table S1, entries 1-3). However, an exceptional M_n of 82 kg/mol with 96% yield for PEDOTF was obtained during the fourth cycle when the reaction time was extended to 3 h (Table S1, entry 4). This might be attributed to the steric bulkiness of NDA preventing aggregation of the Pd catalyst, which leads to higher M_n given longer reaction times, yet results in a slower reaction rate in the early stage.[30] Moreover, this result, along with the result from Table 1, Cycle 4, further confirm the high catalytic performance of Silia*Cat*® DPP-Pd even after being recovered and reused for 3 cycles.

Table 2. Further optimization of the recycling experiments using Silia*Cat*® Pd-DPP using DArP conditions depicted in Scheme 2.[a]

	cycle 1	cycle 2	cycle 3	cycle 4	cycle 5
reaction time (h)	0.5	0.5	1.5	2	36
catalyst recycled (%)	-	98	94	92	91
M_n (kg/mol)	28	22	25	28	23
Đ	2.1	2.0	2.2	2.1	2.2
yields (%)	93	92	91	93	92

[a] All polymerizations were conducted using the general conditions shown in Scheme 2. Detailed experimental procedure can be found in the SI (Section 3).

We have also found that through fine-tuning of reaction times for each cycle, batch-to-batch variations of CP synthesis can potentially be minimized (Table 1, entries 3, 4, 7, 8). For further studies, the carboxylic acid additive was changed back to PivOH since better results were obtained with PivOH for the first two cycles (Table 1, entry 1, 2). Importantly, the second round of catalyst-recycling experiments showed great reproducibility for the first two cycles with same reaction times (0.5 h) compared to those of the first round (29 kg/mol, 23 kg/mol, respectively), offering highly similar M_n (27 kg/mol, 21 kg/mol, respectively for Table 1, entry 5 and 6). For the third cycle, the reaction time was increased to 1.5 h, which afforded PEDOTF with M_n of 26 kg/mol and yield of 90% with minimal variation compared to the first two cycles (Table 1, entry 7). When the reaction time was further increased to 3 h for the fourth cycle, a much higher M_n of 63 kg/mol was provided accompanied by a high yield (95%). Lastly, we tested the recyclability of Silia*Cat*® DPP-Pd for a fifth cycle (Table 1, entry 9), which offered PEDOTF with a satisfactory M_n of 12 kg/mol and yield of 89% using a prolonged reaction time (24 h).

Recycling Silia*Cat*® DPP-Pd for 5 batches of CP synthesis with good to high M_n using DArP is an unprecedented result, since this heterogenous catalyst was only previously recycled up to 3 times in Suzuki cross-coupling reactions with a considerable loss observed in activity after the initial run.[25] However, we envisioned that the large variations of DArP results from the last two cycles (Table 1, entry 8, 9) could be minimized by the further optimization of reaction times. As shown in Table 2, cycle 1-3 of Table 2 employ the same reaction conditions used for Table 1, entries 5-7 with highly similar results. Decreasing the reaction time for the fourth cycle from 3 h (Table 1, entry 8) to 2 h (Table 2, cycle 4) afforded PEDOTF with M_n of 28 kg/mol with little variation from the previous 3 batches. Extending the reaction time for the fifth cycle from 24 h to 36 h improved the M_n to 23 kg/mol. The average M_n of the 5 batches of CPs from Table 2 was calculated to be 25 kg/mol with a small standard deviation (±2.5 kg/mol), which is promising for continuous flow methods of CP synthesis on industrial scales.[33]

Cost analysis was performed (see section 4 of the SI for details), which showed a much lower cost by employing the novel heterogenous approach (only costs \$0.67 of Silia*Cat*® DPP-Pd to synthesize a total of 1.67 mmol of PEDOTF across 5 batches) compared to the conventional homogenous DArP method (\$1.79 of $Pd(OAc)_2$ would be required) to synthesize the same total amount of polymer (assuming the same yields). Another important advantage of recycling heterogenous catalysts for multi-batch CP synthesis is the impact on sustainability by reducing the waste of precious Pd metal. The amount of Pd required to prepare a total of 1.67 mmol of PEDOTF across 5 batches (Table 2) was calculated to be 0.02 mmol (section 4 of the SI), which was significantly lower compared to the conventional homogenous approach (0.084 mmol of Pd). These advantages shed light on the promising potential of extending the newly developed DArP protocol disclosed in this study to continuous flow chemistry for CP synthesis. Although continuous flow synthesis of CPs via DArP has been reported, expensive homogenous Pd catalysts were pumped through the column reactors in the mobile phase, which resulted in significant waste of the Pd species.[34,35] Conversely, the heterogenous approach for DArP developed in this study offers great potential for truly low-cost flow chemistry by allowing the expensive Pd catalyst to be packed in the stationary phase and used continuously throughout the CP production process with a gradually decreasing flow rate.[27] The introduction of a co-solvent in addition to DMA, such as sustainable non-polar solvent CPME or p-cymene, will likely enhance the solubility of CPs during their industrial production in flow. Such strategy (a DMA:CPME = 1:1 co-solvent system for DArP) has been proven effective for the large-scale batch synthesis of a CP as conductive cathode binder for lithium-ion batteries.[4]

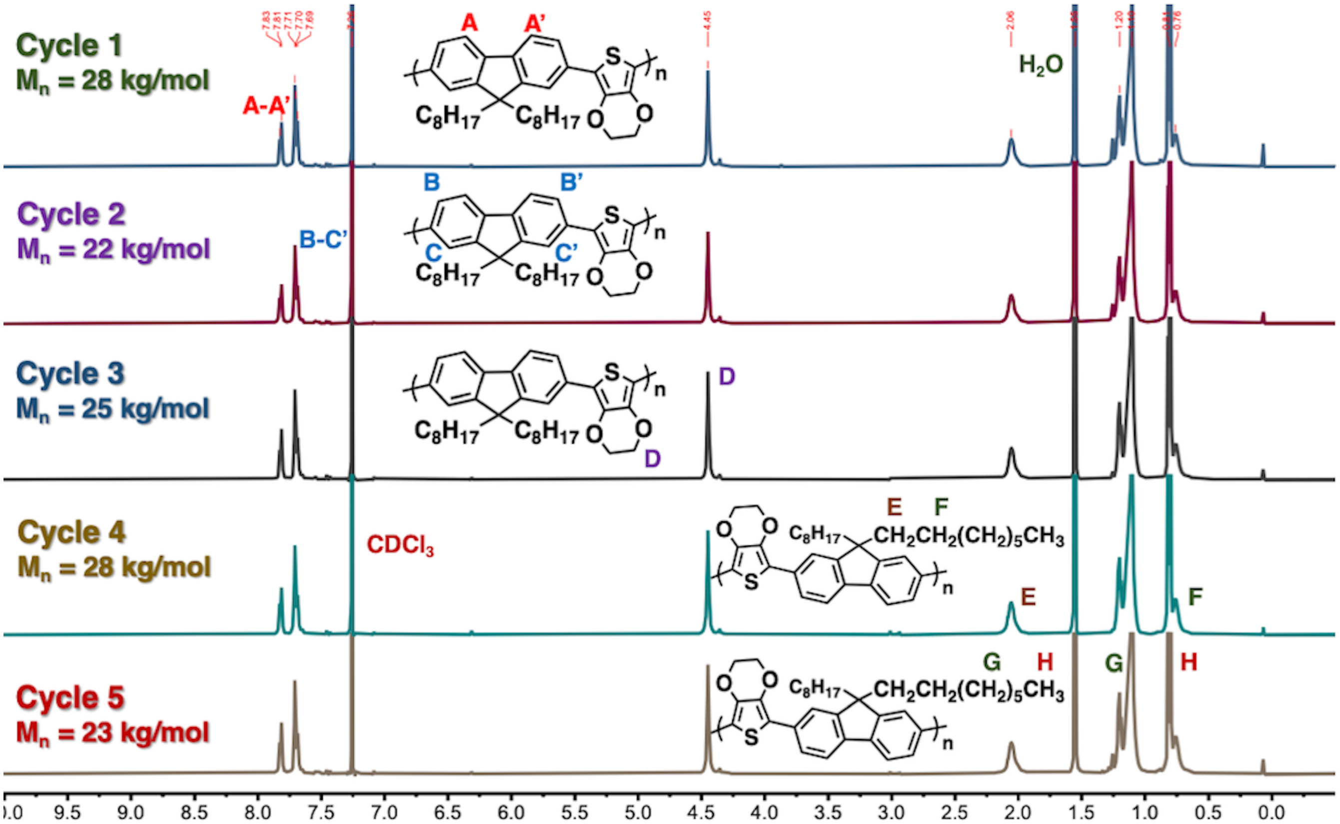


Figure 1. ^{1}H NMR analyses of 5 batches of PEDOTF synthesized from the recycling of Silia*Cat*® Pd-DPP (Table 2). Major resonances (A-H) are denoted. Collected in $CDCl_3$ at 25 °C and 600 MHz.

Other commercially-available heterogenous Pd catalysts besides Silia*Cat*® DPP-Pd were also evaluated. The polypropylene fiber-supported Pd complex FibreCat® has received attention for its good catalytic efficiency in Suzuki coupling protocols with good recyclability (up to 5 times).[36,37] By replacing the Pd source with FibreCat® using reaction conditions listed in Scheme 2 and Table 2, we found that recycling FibreCat® for 5 batches of PEDOTF was feasible, however, with much lower M_n (1.8-4.7 kg/mol) and yields (Table S2). This could be explained by the much lower reactivity of FibreCat® under the DArP conditions utilized in this study, which was evidenced by control experiments using 24 h of reaction time showing that lower M_n (7.7 kg/mol) of PEDOTF was afforded using pristine FibreCat® compared to that by pristine Silia*Cat*® DPP-Pd (M_n = 29 kg/mol) in only 0.5 h (Scheme S3 and Table 1). Pd/C is one of the most widely employed commercial solid-supported catalysts for cross-coupling reactions, and has been successfully used in DArP protocols.[17,19] However, the effectiveness of carbon-supported Pd catalysts is found to be reliant on the leaching of Pd into the solution, which significantly limits the recyclability of the catalyst.[16,38,39] Indeed, although we found Pd/C to be effective for the synthesis of PEDOTF via DArP (24 h of reaction time was needed to afford M_n of 40 kg/mol, see Scheme S2, Table S2), the catalyst was not reusable after recovering from the initial run.

Polymer structural analysis was performed by using ^{1}H NMR spectroscopy. Major resonances (Figure 1, A-H) for all polymers were identical to literature reports.[30,31] Detailed ^{1}H NMR analysis (Figure S17) showed the absence of polymer structural defects such as donor-donor homocouplings. Figure 1 demonstrates the identical ^{1}H NMR spectra of 5 batches of CPs synthesized by recycling Silia*Cat*® Pd-DPP 5 times (Table 2), which confirms minimal batch-to-batch structural variation with this novel heterogenous protocol for DArP. UV-vis absorption spectra of these 5 batches of CPs were also identical with each other (Figure S21) and consistent with reported spectra (Figure S18-23).[30]

In conclusion, an approach for sustainable multi-batch CP synthesis is presented for the first time by the recycling of heterogenous catalysts via DArP. The exceptional reactivity and recyclability of Silia*Cat*® Pd-DPP for DArP was highlighted by affording PEDOTF with M_n up to 82 kg/mol even after recycling of the catalyst 3 times. Through optimization of reaction conditions, up to 5 batches of polymers were obtained by the recycling of the same Pd catalyst, offering a minimization of batch-to-batch variations across all batches (25±2.5 kg/mol). Though DArP is intrinsically the most sustainable protocol to prepare CPs, this work addresses among the most significant limitations of prevailing DArP methods by prolonging the lifetime of the expensive Pd species through adapting a novel heterogeneous approach, which is highly promising for low-cost continuous flow CP synthesis on industrial scales. As an initial demonstration of this new concept for DArP, this report only focused on the synthesis of a representative polymer (PEDOTF) with Fagnou-derived conditions using commercial heterogenous catalysts. Future studies will focus on expanding the scope of the methodology by the further optimization of reaction conditions, exploration of the employment of sustainable solvents for CP synthesis, and design novel heterogenous catalysts that exhibit higher efficiency and superior recycling properties.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures including the synthesis and characterization for all monomers and polymers are included in the supporting information (SI). This material is available free of charge via the internet at http://pubs.acs.org.

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